Quantitative rotational to librational transition in dense H2 and D2

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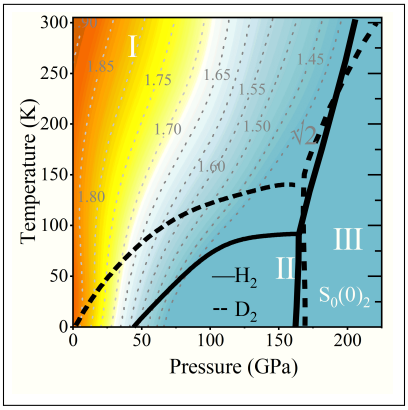
Hydrogen,phase I, Raman spectroscopy, Roton, libron

Abstract

Raman spectroscopy demonstrates that the rotational spectrum of solid hydrogen, and its isotope deuterium, undergo profound transformations upon compression while still remaining in phase I. We show that these changes are associated with a loss of quantum character in the rotational modes, ie. with increasing pressure, the angular momentum J gradually ceases to be a good quantum rotational number. Through isotopic comparisons of the rotational Raman contributions, we reveal that hydrogen and deuterium evolves from a quantum rotor to a harmonic oscillator. We find that the mechanics behind this transformation can be well described by a quantum mechanical single inhibited rotor, accurately reproducing the striking spectroscopic changes observed in phase I.

Graphical TOC Entry



Dense hydrogen is an archetypical system in condensed matter science, being the simplest molecular solid it is a fascinating subject of investigation revealing insights into fundamental quantum mechanical concepts.[1–6] At low temperature and pressures, molecular hydrogen (H_2) and deuterium (D_2) form simple molecular solids with a hexagonally close-packed (hcp) structure, phase I. Within this phase, at the lowest temperatures (<10 K), spectroscopy shows that the molecules behave as free rotors.[7] Such behaviour is impossible in classical physics, where rotational motion must cease at zero temperature. As such, phase I is considered a quantum solid with molecules characterised by angular momentum quantum number J. Within the neighbouring boundaries between phase I, phase II (II'), and phase III;[2,7–15] the intermolecular interactions are strong enough that J would no longer be a good rotational quantum number. However, the change from rotor to libration has yet to be identified.

Spectroscopy has been the main diagnostic in identifying new phase transitions in the dense hydrogens, with the pressure/temperature induced changes of the main intramolecular vibrational mode (vibron) being the primary indicator.[11] Surprisingly, there has been little attention paid to the rotational spectrum of the hydrogens, and the fact that in phase I (and the liquid state) the rotational modes change shape on compression (Figures 1- 2). The nature of hydrogen, whether a rotor or a harmonic oscillator, cannot be directly measured from its Raman excitations, the energy of the quantum levels, but can be deduced through the isotopic comparison, $\omega_{H_2}/\omega_{D_2}$, for a given pressure. For a rotor $\omega_{H_2}/\omega_{D_2} = 2$, whereas for an oscillator the frequency ratio is expected to be $\omega_{H_2}/\omega_{D_2} = \sqrt{2}$.

In this work, we have conducted high-resolution Raman experiments through isothermal compressions of mixed $ortho - para$ H_2 and D_2 at 10, 80, 150 and 300 K. With fast cooling from the room temperature the equilibrium ortho-to-para ratio in hydrogen and deuterium $3:1$ and $1:2$, respectively. The Raman shift of the rotational modes as a function of pressure allow us to establish the H_2/D_2 mass scaling laws as the density increases. We show that within phase I, J gradually ceases to be a good quantum number to define the

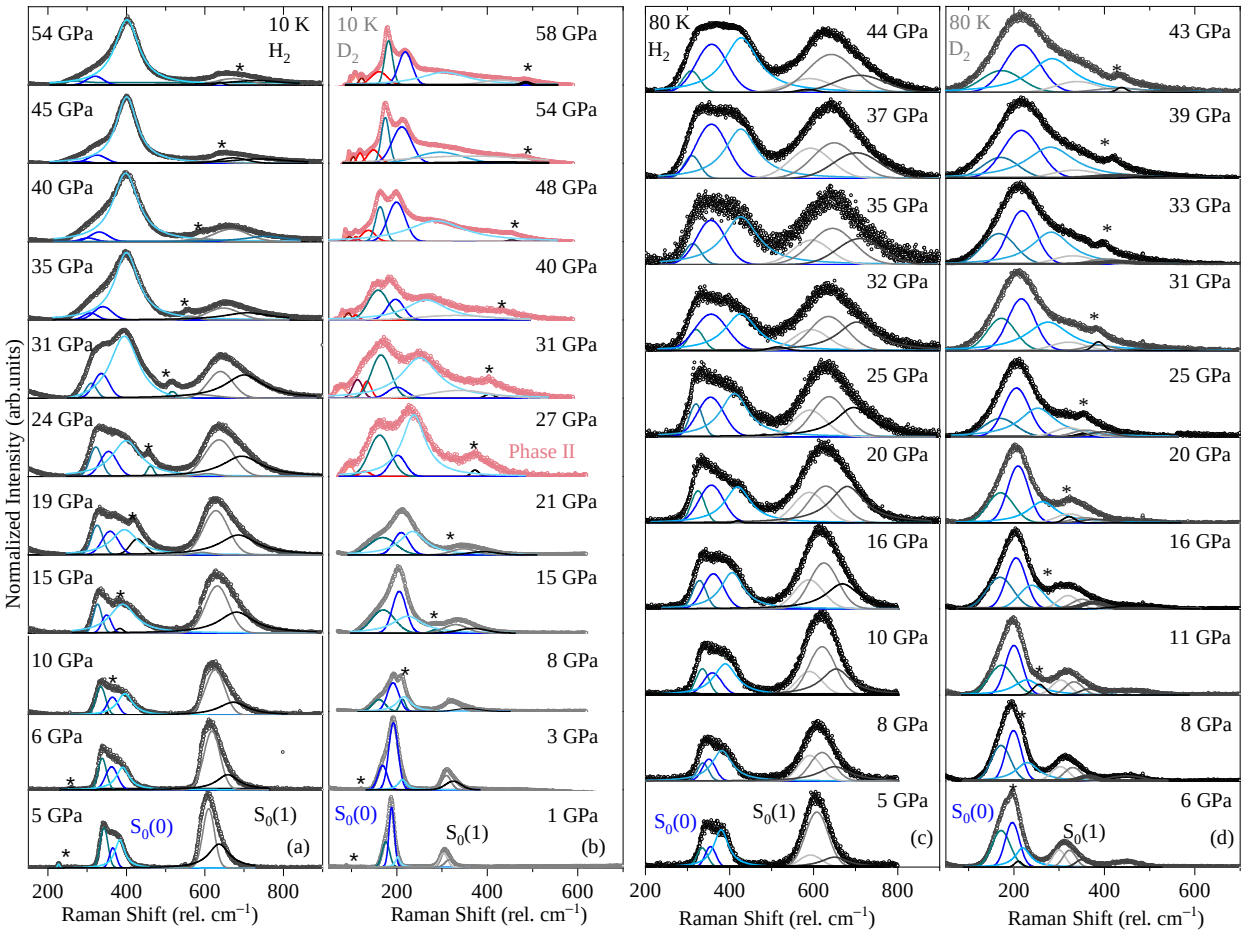


Figure 1: Representative Raman spectra during isothermal compression paths. a) At 10 K to maximum pressure of 54-58 GPa of hydrogen; b) deuterium, which at 26 GPa undergoes a transition to phase II (II'[8]) marked by the new contributions in red. c) at 80 K up to 44 GPa of hydrogen; d) deuterium up to 43 GPa. $S_0(0)$ is fitted to three contributions in blue: the low energy level corresponding to $m = \pm 1$, the middle one to $m = \pm 2$ and the higher one to $m = 0$. $S_0(1)$, in grey, is fitted to two contributions for 10 K isothermal compressions and to three for the 80 K ones. Where visible, E_{2_g} phonon is marked with $*$ symbol.

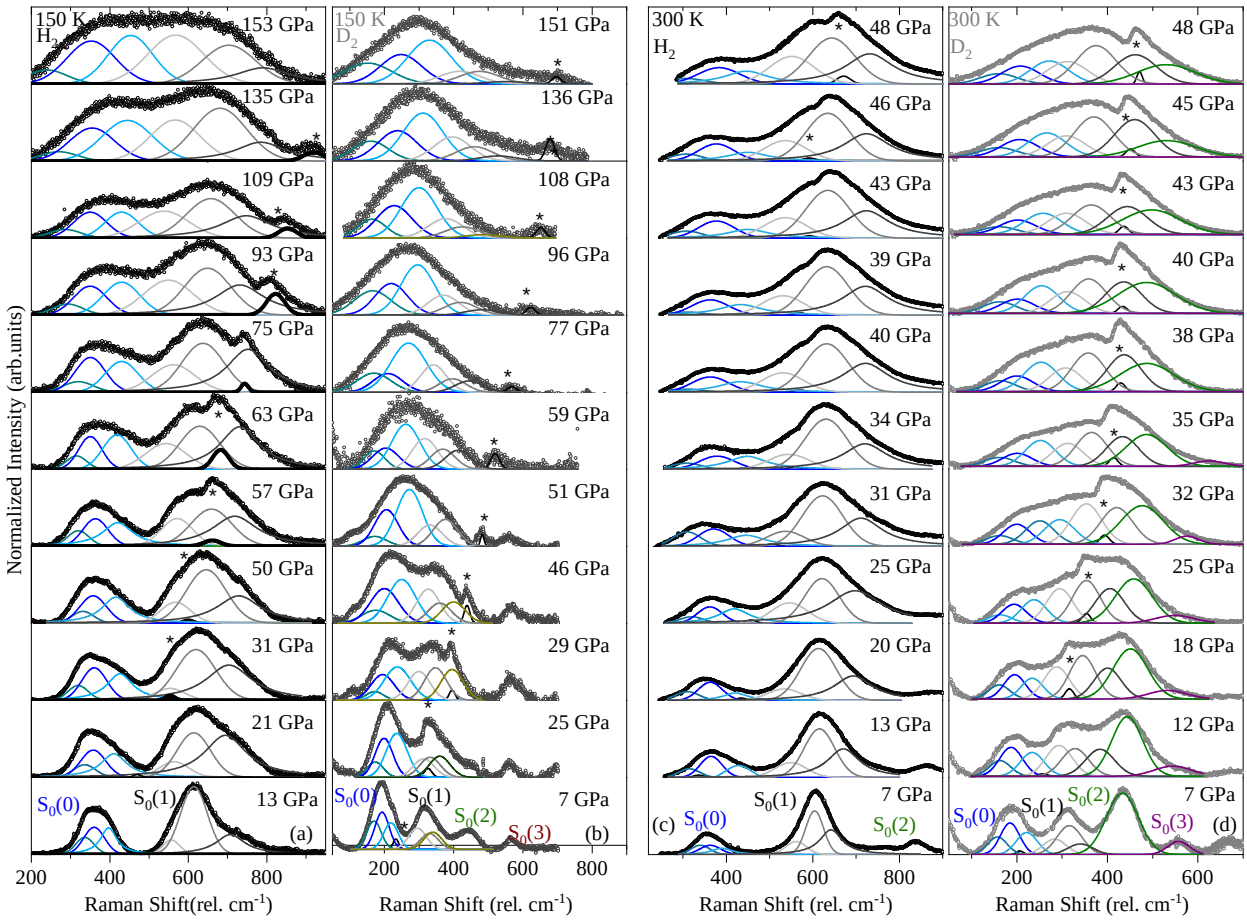


Figure 2: Representative Raman spectra during isothermal compression paths. a) At 150 K to a maximum pressure of 150 GPa of hydrogen; b) deuterium. c) At 300 K to a maximum pressure of 48 GPa of hydrogen; d) deuterium. $S_0(0)$ is fitted with three contributions in blue: the low energy level corresponding to m=±2, the middle one to m=±1, and the higher one to m=0. $S_0(1)$ is fitted to three contributions. Where visible, phonon E_{2g} mode is marked with * symbol.

rotational freedom of the molecules, and phase I transforms iso-structurally from a quantum to a classical solid.

The low-frequency regions of the Raman spectra of H_2 and D_2 exhibit the E_{2_g} lattice phonon and the rotational modes: $S_0(0)$ $\Delta J = 0 \rightarrow 2$, $S_0(1)$ $\Delta J = 1 \rightarrow 3$, $S_0(2)$ $\Delta J = 2 \rightarrow 4$.As seen in Figures 1 and 2, each of the rotons exhibit a different number of contributions as the crystal field within the solid structure lifts the degeneracy of the J levels.[3,16–18] Details of the analysis and fitting parameters of the different contributions are gathered in Figures S1-S6. In Figure 1, for deuterium at 10 K and above 29 GPa, we see the phase II transition, characterised by the appearance of lower frequency modes overlapping with $S_0(0)$ and the *hcp*-E_{2_g} optical phonon.[8] The detailed study of this phase is out of the scope of this work and the assignment of the modes within deuterium phase II is tentative.

The intensity of the rotational modes are dependent on temperature, where there is a redistribution of Raman intensity to higher order rotational bands with increasing temperatures.[19] H_2 molecules exist in spin isomers of ortho- (nuclear spin equals 1 ($I = 1$) and para- ($I = 0$). In order for the total H_2 molecular wave function to be antisymmetric under exchange of atomic positions, Pauli's exclusion principle demands that for the rotational ground state $J = 0$, the corresponding total nuclear wave function is antisymmetric (singlet state of $I = 0$). For the $J = 1$ rotational state, the total nuclear wave function is symmetric (triplet state of $I = 1$). Therefore, the spin allotropic isomerism of the H_2 molecule originates in the coupling of both rotational properties and nuclear spin orientations. As such, the intensity ratio of the rotons are intimately related to $ortho-para$ concentration and have been used in previous works to quantitatively evaluate the $ortho - para$ conversion rate.[3,20] This rate strongly depends on temperature, pressure, and isotope, with the the conversion rate faster for H_2 than for D_2.[20] As seen in Figure 1 at 10 K and 80 K, the rapid growth of the $S_0(0)$ mode in H_2 as a function of pressure is a manifestation of the increased para conversion at higher density.[20] At higher temperatures (150 K and 300 K), experiments are already conducted in equilibrium and the $ortho - para$ concentration remains constant at

any pressure.

Comparison of the room temperature Raman spectra of H_2 at 7 GPa and 48 GPa shows significant changes, going from sharp and well defined low-frequency contributions to broad and non-symmetric bands centred at a frequency which would imply a physically unreasonable bond length for a quantum rotor (Figure 2). This raises the question of what causes dramatic spectral changes in the rotons, especially considering that the hydrogen's vibrational mode, the E_{2_g} phonon and the crystallographic data all demonstrate a continuity of the hexagonal close-packed structure.[21–28] The pressure-induced broadening is a manifestation of the decrease in the lifetime of the rotations.[18] Unfortunately, the width of the roton cannot be used to determine the precise conditions in which a roton to libron transition happens, as the impeded rotation is observed as a continuous peak broadening without discontinuities (Figures S3 and S5).

Due to the influence of the crystal field on the hexagonal structure, the degeneracy of the rotational levels is lifted and the $S_0(0)$ splits into three lines: $m = \pm 1$, $m = \pm 2$ and $m = 0$; while $S_0(1)$, $\Delta J = 1 \rightarrow 3$, comprises eight modes: $m = \pm 1, 0$ from $J = 1$ and $m = 0, \pm 1, \pm 2, \pm 3$ from $J = 3$. We can resolve the three contributions of $S_0(0)$ at the lowest temperatures though the well defined spectral features (Figure 1), the second derivative analysis (Figure S1) and theoretical calculations (Figure S2). The ideal configuration for the (2:2:1) intensity ratio between the $S_0(0)_2$, $S_0(0)_1$ and $S_0(0)_0$ is altered (see Fig. 1), what has already been attributed to $ortho - para$ effects,[3,18] textcolorblueand to crystal orientation and spectroscopic configuration.[18] Comparatively, the $S_0(1)$ mode is not as well resolved, even at 10 K when the thermal broadening is minimized. As such, we fit $S_0(1)$ with two contributions at 10 K (because of its low intensity) and to three contributions at all other temperatures (Figures S3-S6 gather full-width half-maximum and area used in the fitting of $S_0(0)$ and $S_0(1)$). On compression, the splitting between the different contributions increases due to intermolecular interactions, which may be steric or electric quadrupole-quadrupole (EQQ).[3,16–18] In Figure 3 it is seen, that for all the measured temperatures, increasing

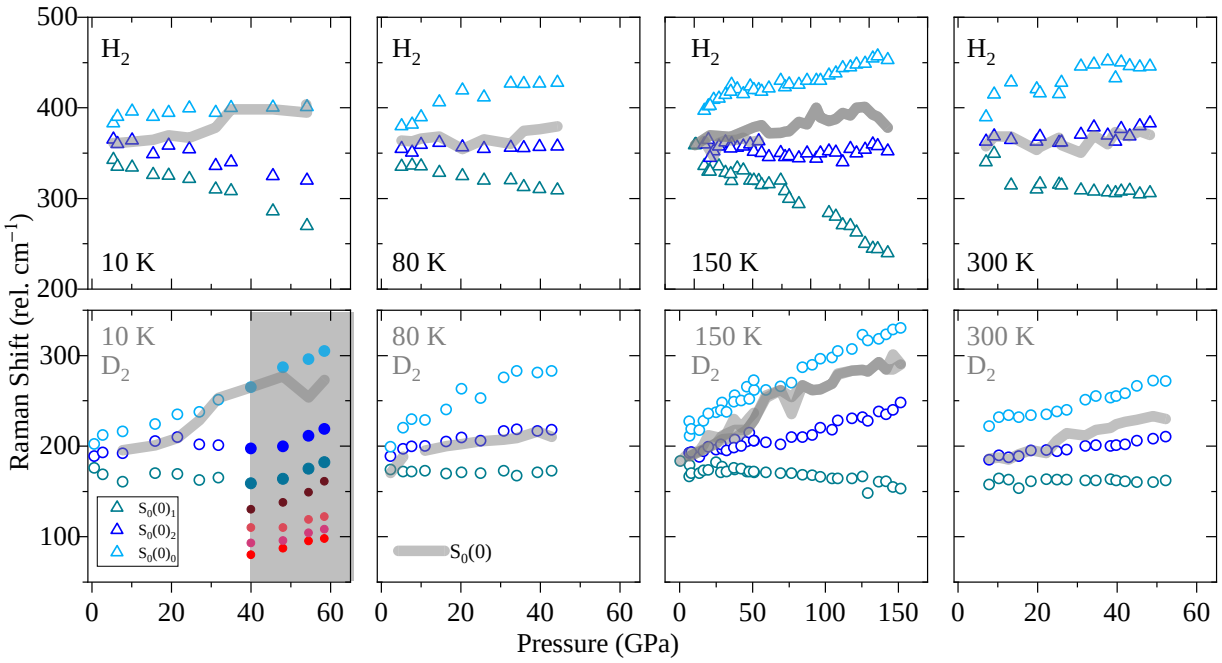


Figure 3: Raman shift for the $S_0(0)$ contributions as a function of pressure of H_2 (top panel) and D_2 (bottom panel). Red points in the panel of D_2 at 10 K correspond to the characteristic features of phase II (II').[8] Grey thick line is Raman shift obtained from fitting the S_0 as a single contribution (Figures S7-S8).

pressure yields a significant splitting of about 200 cm^{-1} between $m = \pm 2$, $m = \pm 1$, and $m = 0$ at 50 GPa for both isotopes. This splitting becomes more pronounced on further compression above 50 GPa (as observed for the 150 K isothermal compressions).

The splitting of the $S_0(0)$ triplet has been observed in previous experimental works and has been interpreted in various ways: as a single contribution, obviating force field effects;[24,29] as two contributions with no physical explanation[23,29] and only in some cases the lifting of the degeneracy has been taken into account.[2,30,31] In all cases, a robust analysis of the rotational modes for both of the isotopes at different isothermal compression paths was missing.[23,24] This lack of consistency in the analysis of $S_0(0)$, exacerbated by the different pressure dependence of the three modes, has prevented the understanding of pressure effects into the validity of J within phase I and any possible rotational to librational transition.

We have analysed in detail the evolution of the ratios between the different $S_0(0)$ contri-

butions of H_2 divided by those of D_2 ($\omega_{H_2}/\omega_{D_2}$) as a function of pressure (see Figure 4). We observe that the relationship of $\omega_{H_2}/\omega_{H_2}$=2 within the free rotor approximation is fulfilled at low pressures, however, as pressure is increased the trend deviates towards the harmonic oscillator ratio of $\omega_{H_2}/\omega_{D_2}$=$\sqrt{2}$. This trend is also obtained when analysing the $S_0(1)$ contributions (Figure S9-S10). This transition is expected if the harmonic oscillators, crystal structure, and volume are the same for the two isotopes ($\sqrt{m_{H_2}/m_{D_2}}$).

For comparison, we have also calculated the $\omega_{H_2}/\omega_{D_2}$ values as a function of pressure ignoring the splitting due to pressure-induced degeneracy lift of the m_j levels, and taking a single frequency for the $S_0(0)$ modes, represented by grey symbols in Figure 4 (see Figures S7-S8 for fittings). Importantly, when the same approach is used for both isotopes, the roton to libron transition is present regardless which rotational mode is used and whether mode splitting is included, as long as both isotopes are approached on the same way.

To ensure these results are independent of the fitting, we have also analysed the E_{2_g} phonon. The E_{2_g} mode is well defined, even though at certain pressures and temperatures it overlaps with rotational modes, e.g. at 300 K and 48 GPa (Figure S11). In agreement with previous results, the trend of the E_{2_g} phonon as a function of pressure is invariant with temperature (see Figure S11).[2,23,24,29,32] Figure 4 shows the frequency ratios between the H_2/D_2 E_{2_g} phonon, and only small deviations from the $\omega_{H_2}/\omega_{D_2}$=$\sqrt{2}$ trend is observed with increasing pressure. This deviation has been previously attributed to the anharmonicity of the intermolecular potentials.[24]

Interestingly, we find that the rate at which the rotons deviate towards the libron limit is temperature dependent (see Figure4). While at 10 K the experimental $\omega_{H_2}/\omega_{D_2}$ ratio crosses the $\sqrt{2}$ line at around 40 - 60 GPa, extrapolation of the experimental $\omega_{H_2}/\omega_{D_2}$ values for the other isothermal compression runs indicate that the $\sqrt{2}$ line is crossed at higher pressures with increasing temperature. For example, $S_0(0)_0$ would cross the $\sqrt{2}$ at 80 K around 80 GPa, while at 150 and 300 K these would cross around 160 - 170 GPa. This can be explained by the loss of correlation between adjacent molecules making the local environment

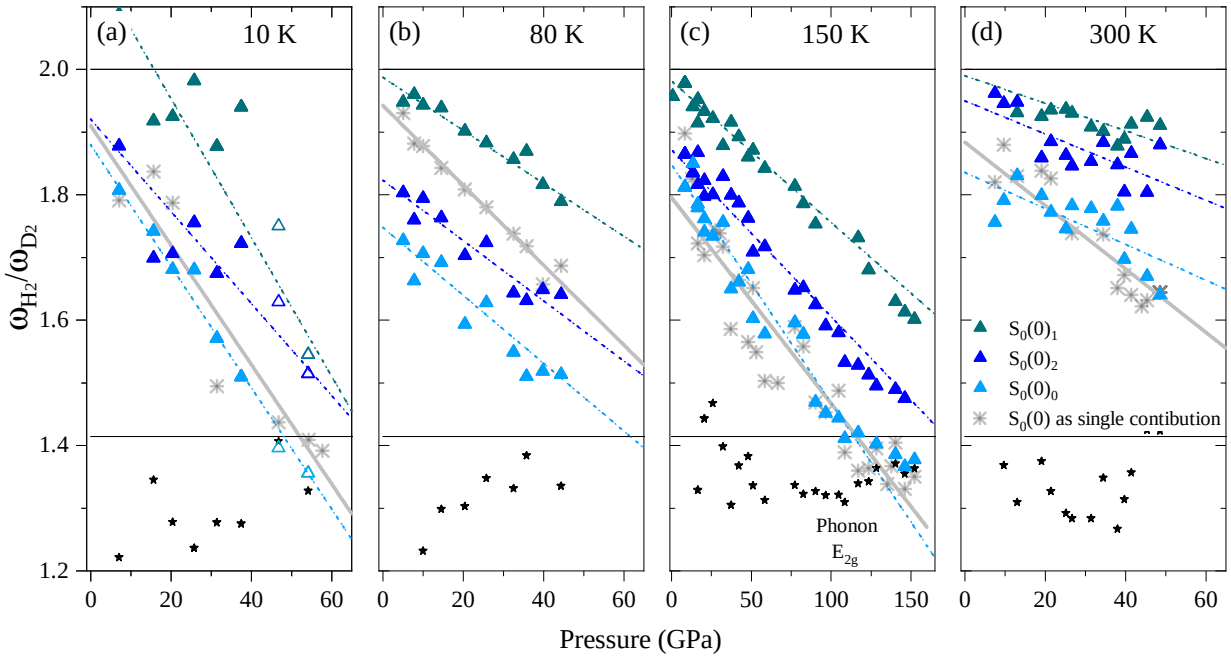


Figure 4: Pressure dependence of $S_0(0)$ ratios, $\omega_{H_2}/\omega_{D_2}$, for isothermal compression experiments at a) 10 K, b) 80 K, c) 150 K and d) 300 K.. The horizontal lines mark the ratio in a pure harmonic oscillator, at $\omega_{H_2}/\omega_{D_2}=\sqrt{2}$, and pure rigid rotor ratio $\omega_{H_2}/\omega_{D_2}=2$. Colour triangles represent the ratio of each contribution of the $S_0(0)$ mode and coloured lines mark their respective linear fit. The empty triangles refer to the ratios within D_2 phase II (II'). [8] Black stars correspond to the phonon ratios. Grey stars represent the ratios obtained disregarding $S_0(0)$ degeneracy lifting (Figure S7-S8)

more homogeneous. [18] Particularly compelling is the fact that when inserting these pressure values within the overlapped H_2 and D_2 phase diagram (Figure 5) they fit between the phase transitions I to II and I to III (a description of the contour plot interpolation is provided in the supporting materials). These results imply that the $roton-libron$ transition occurs as an intermediate to facilitate the structural changes between low pressure phase I, considered a pure quantum phase, towards phase II and III. Intriguingly, we observe that the different contributions of $S_0(0)$ gradually become librons at different rates, where the $S(0)_0$ from $m=0$ seems to be the one which crosses the boundary first (Figure S12-13), implying that rotation in the plane persists to higher pressures. [18] Transitions from phase I to II and to III is marked by a gradual change of the H_2 rotational freedom, which disappears along the isothermal path, adopting a harmonic oscillator character.

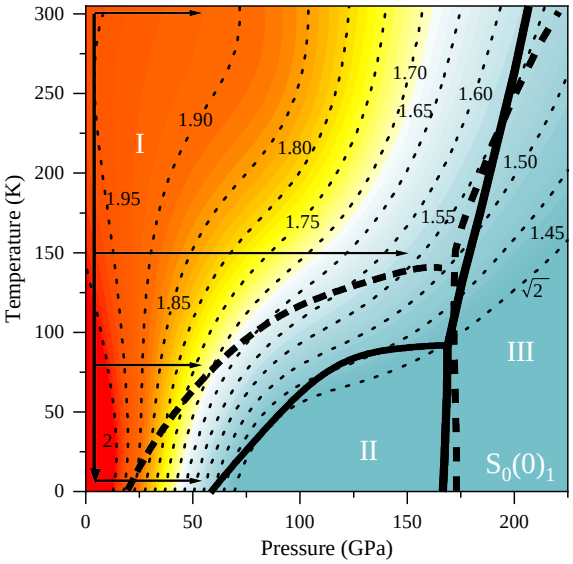


Figure 5: H_2 and D_2 phase diagrams represented with solid and dashed lines respectively, taken from Ref.[Liu2017]. Contour curves represent the change in the $\omega_{H_2}/\omega_{D_2}$=2 to $\sqrt{2}$ for the $S_0(0)_1$) contribution. Arrows are used to indicate the experimental paths followed here, typically cooling fast with a subsequent isothermal compression.

Comparison between H_2 and D_2 reveals that there is a continuous transformation of vibrational character across phase I. Complete transformation is observed experimentally at 10 K around the phase I to phase II boundaries. The transition from a free rigid rotor to a harmonic oscillator implies the loss of J as a good quantum number to define the rotational freedom of H_2 and D_2. It is also demonstrated that the standard isotope effects due to the quantum zero-point oscillations remain important up to the phase III transition.

Acknowledgements

M.P.A. GJA and EG acknowledge the support of the European Research Council Grant Hecate Reference No. 695527. VA. would like to acknowledge SUPA for her Ph.D. research grant. Funding has been provided by the respective Chinese "1000 Talent Award" grants of both PDS and RTH. XDL acknowledges the support of the National Science Foundation of

China (Grant No. 11874361).

Supporting Information Available

The Supporting Information is available free of charge at `https://`

- Methods.
- Second derivative analysis, Theoretical Raman shift of the $S_0(0)$ and $S_0(1)$ contributions, fitting parameters (Full width half maximum and areas). Fitting of the spectra not accounting for splittings. Phase diagram from different rotational S_0(contributions).

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